

Electronic Supplementary Information (ESI) for

# Novel Tri-Block Copolymer of Poly (acrylic acid)-*b*-poly (2,2,3,3,4,4,4-hexafluorobutyl acrylate)-*b*-poly (acrylic acid) Prepared via Two-Step RAFT Emulsion Polymerization

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## Experimental

### Materials

Acrylic acid (AA; >99%; Beijing Chemical Works), 1,4-dioxane (>99%; Beijing Chemical Works), 4,4'-azobis (4-cyanovaleric acid) (ACVA; >98%; Damas-beta), hexafluorobutylacrylate (HFBA; >98%; Xeogia), Carbondisulfide (>98%; Aladdin), acetone (>99%; Beijing Chemical Works), and Sodium hydroxide (>99%; Beijing Chemical Works) were used as received without further purification. Deionized water was prepared in our laboratory. The RAFT agent, S,S'-bis (R,R'-dimethyl-R''-acetic acid)-trithiocarbonate (BDAAT), was synthesized and purified as described in Ref. 1.

### Synthesis of S,S'-bis (R, R'-dimethyl-R''-acetic acid) trithiocarbonate (BDAAT)

Carbon disulfide (27.4 g, 0.36 mol), chloroform (107.5 g, 0.9 mol), acetone (52.3 g, 0.9 mol), and tetrabutylammonium hydrogen sulphate (2.41 g, 7.1 mmol) were mixed with 120 mL mineral spirits in a 2 L jacketed reactor cooled with tap water under nitrogen. Sodium hydroxide (50%) (201.6 g, 2.52 mol) was added dropwise over 90 min, the temperature was kept below 25 °C. The reaction was carried out overnight with stirring. Then 900 mL water was added to dissolve the solid, followed by 120 mL concentrated HCl to acidify the aqueous layer. Stirred for another 30 min with nitrogen purge. Filter and rinse the solid thoroughly with water. After drying to constant weight, the solid specimen (41.3 g, earth-color) was obtained. After that, further purification by re-crystallization from 60% acetone solution was carried out and the yellow crystalline solid was finally obtained.<sup>1</sup>

### Synthesis of PAA<sub>100</sub>-PHFBA<sub>20</sub>-PAA<sub>100</sub> macro-RAFT agent

The polymerization was carried out in 1,4-dioxane. In the first step, AA monomer (7.2 g, 0.1 mol), RAFT agent (BDAAT, 0.141 g, 0.5 mmol), and initiator ((4,4'-azobis (4-cyanovaleric acid), ACVA), 28 mg, 0.1 mmol) were added into 1,4-dioxane (38.92 g). Thus, in the synthesis system, the mole ratio of monomer: RAFT agent: initiator is 100:1:0.1. The mixture was then deoxygenated by nitrogen for 30 min and reacted for 1.5 h at 80 °C. The deoxygenated HFBA (2.36 g, 0.01 mol) was then added and the polymerization was carried out for another 2 h. The obtained solution (48.65 g) was used directly as Macro-RAFT agent.

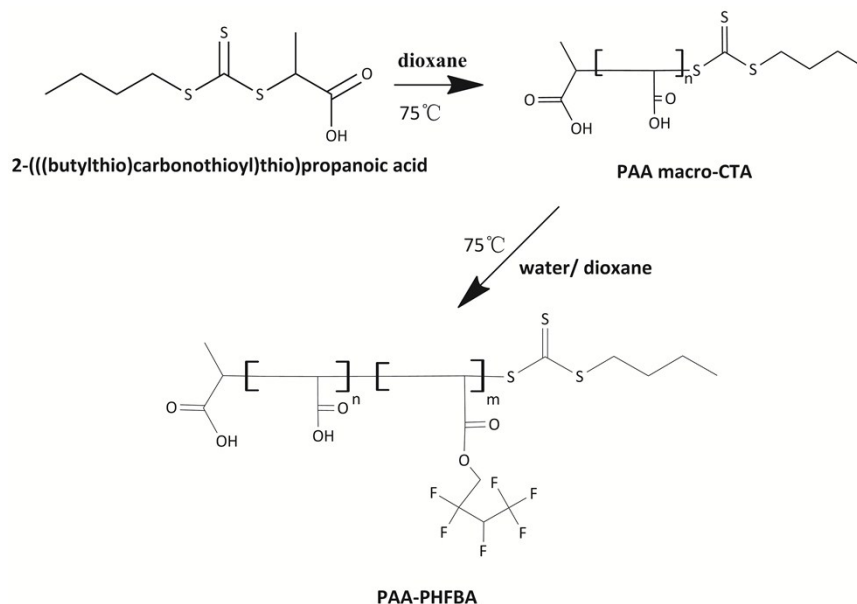
### Synthesis of PAA<sub>100</sub>-PHFBA<sub>400</sub>-PAA<sub>100</sub>

Considering the continuity of reaction and side reaction during desolvent process, the mentioned PAA<sub>100</sub>-PHFBA<sub>20</sub>-PAA<sub>100</sub> Macro-RAFT agent solution is used directly for the further polymerization. The Macro-

RAFT agent solution of PAA<sub>100</sub>-PHFBA<sub>20</sub>-PAA<sub>100</sub> (48.65 g, 0.5 mmol) and initiator (ACVA, 28 mg, 0.1 mmol) were added into deionized water (287.6 g). The mixture was stirred sufficiently and deoxygenated by nitrogen for 30 min. The temperature was increased to 75 °C. The deoxygenated HFBA monomer (47.2 g, 0.2 mol) was then added at a constant rate until the reaction was finished.

#### Synthesis of PAA-*b*-PHFBA di-block copolymers

The PAA-PHFBA di-block copolymers were prepared as shown in Scheme S1.



Scheme S1: detailed molecular information about the di-block copolymer.

#### Latex film preparation

The latex film was prepared with self-made 8cmX6cm mould and biaxial oriented polypropylene (BOPP) film was used as substrate. The latex (20 g) was used to prepare the film by casting on polypropylene substrate at room temperature for 12 h. The cast latex films were kept in a vacuum oven at room temperature until constant weight was reached, in order to evaporate the solvent and water completely. The as-prepared latex films were held in the vacuum dryer at room temperature until measurements.

#### Monomer conversion

The results of monomer conversion were measured by gravimetric analysis according to Ref. 2.

#### Molecular weight and PDI

The molecular weight and PDI of the synthesized tri-block copolymers were analyzed at 30 °C by using a GPC 515-2410 of Waters Corporation (Milford, MA) that consists of an HPLC Pump and Refractive Index Detector. THF was used as the mobile phase at a flow rate of 1 mL/min. The THF solution of polymers was injected at a concentration of 3 mg/ml after filtration through a 0.45 μm microporous membrane. The molecular weight of copolymer specimens was calculated with a calibration curve based on polystyrene standards.

#### <sup>1</sup>H-NMR spectra

The <sup>1</sup>H-NMR spectra were measured by NMR spectroscopy (Bruker AV600) in d<sub>6</sub>-DMSO and d<sub>8</sub>-THF solvent at room temperature.

#### Atomic force microscope (AFM)

The AFM images were recorded by Multimode Nanoscope IIIa, Digital Instruments, operated in tapping mode under ambient conditions.

#### Chemical compositions

The chemical composition were measured by X-ray photoelectron spectroscopy (XPS, ESCA Lab 2000, VG Scientific) with a MgKR X-ray source. The X-ray gun was operated at 12 kV and 10 mA, and the analyzer chamber pressure was 10<sup>-8</sup> mbar. The take off angle was fixed at 90°.

#### Fourier transform infrared (FT-IR)

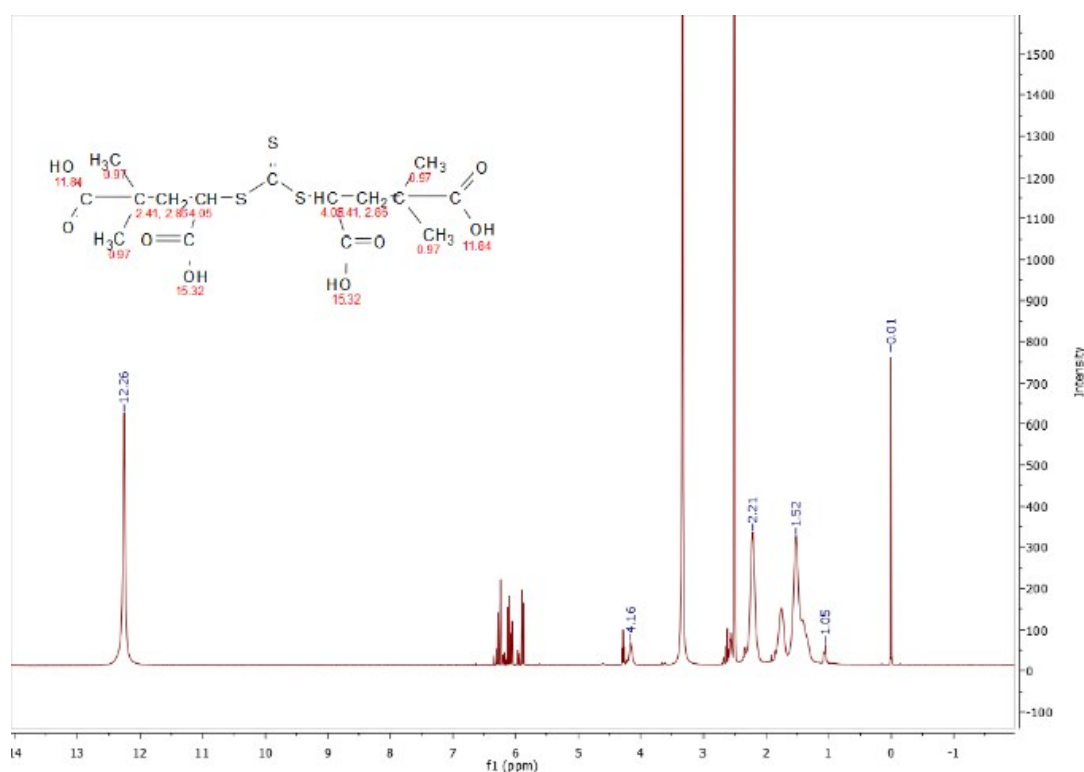
The IR spectra were measured by using a Bruker Tensor 37 Fourier transform IR spectrometer. The resolution was 4 cm<sup>-1</sup> and each sample was scanned for 20 times. The transmission IR spectrum was measured by using PAA-PHFBA-PAA solution via KBr pellet method and the absorbance ATR spectrum was measured by using PAA-PHFBA-PAA film.

#### Water contact angle (WCA)

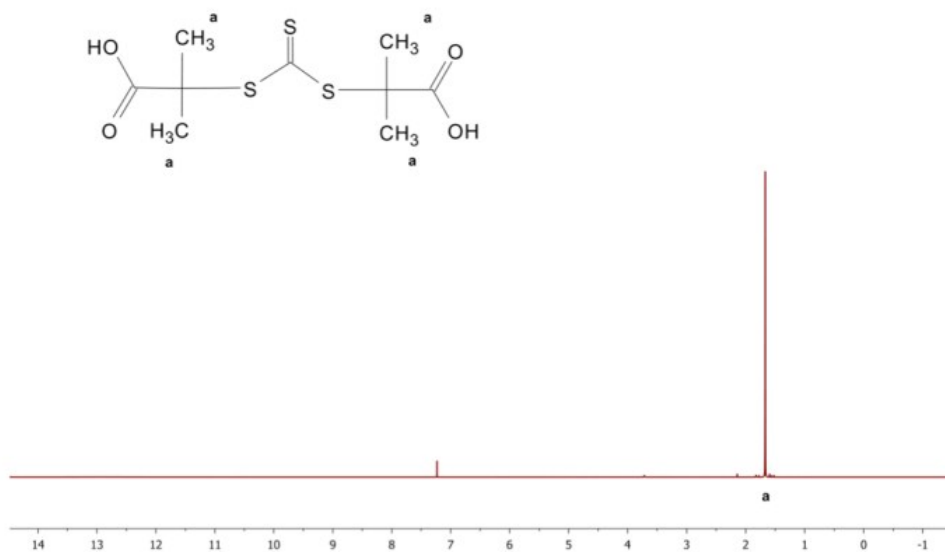
The WCA of synthesized latex films was measured on an OCA20 Contact-Angle System (Dataphysics, Germany) at room temperature. The WCA values were the averages of five independent measurements according to Ref. 3.

#### Tensile properties and hardness

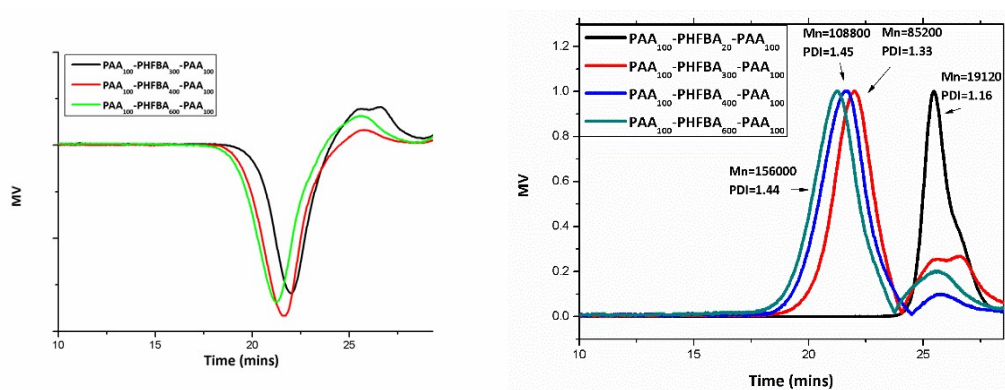
The mechanical property of synthesized latex films was measured according to ASTM-D412 and ASTM-D2240. The testing samples were cut from the latex films. Tensile properties were measured by Instron3300 universal material tester.



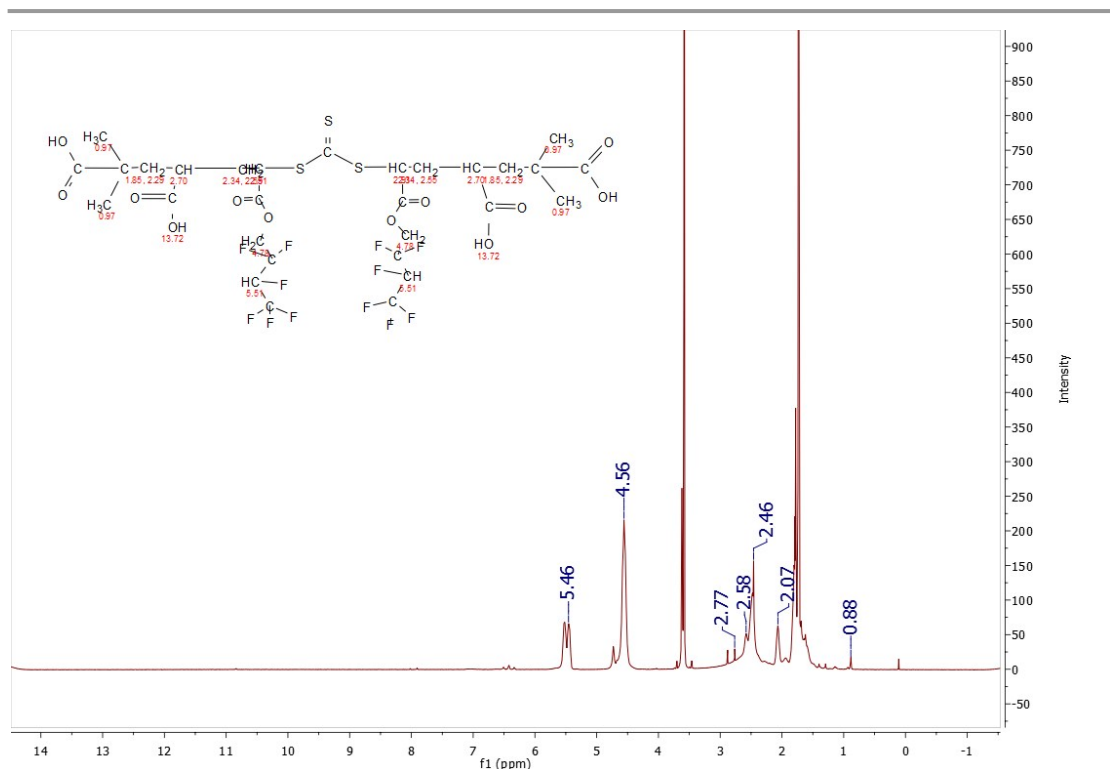
**Fig. S1:** <sup>1</sup>H NMR Spectrum of the synthesized Macro-RAFT agent. PAA<sub>200</sub> (DMSO-d<sub>6</sub>, ppm from TMS): 1.05 (CH<sub>3</sub>), 1.59 (CH<sub>3</sub>), 2.21 (CH<sub>2</sub>-CH), 4.16 (CH), 12.26 (OH), 2.61 (1,4-dioxane), 6.12 (CH<sub>2</sub>=CH).



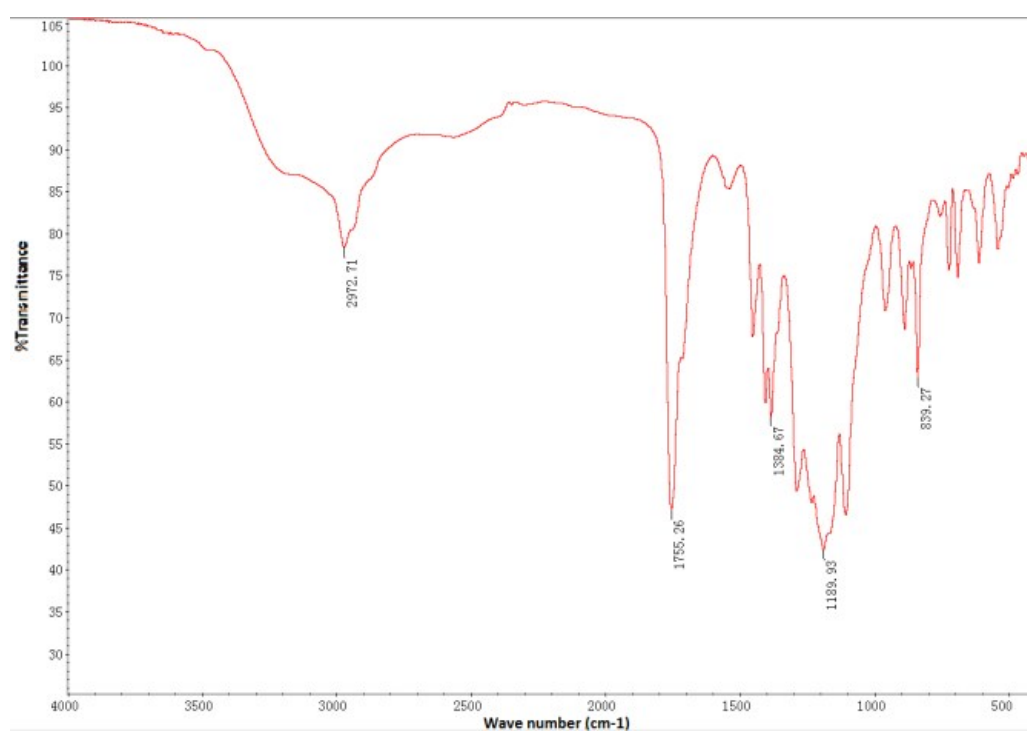
**Fig. S2:**  $^1\text{H}$  NMR Spectrum of BDAAT. (DMSO- $d_6$ , ppm from TMS): 1.59 (s, 12H), 12.91 (s, 2H).



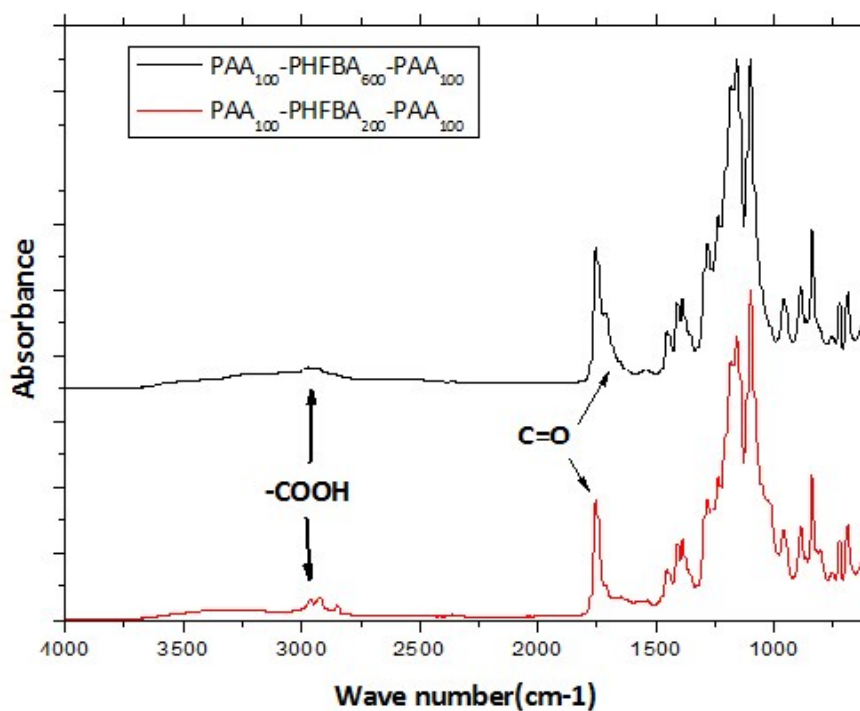
**Fig. S3:** Original (left) and modified (right) GPC curves of macro-RAFT and PAA-*b*-PHFBA-*b*-PAA tri-block copolymers<sup>4</sup>



**Fig. S4:** <sup>1</sup>H NMR spectrum of PAA<sub>100</sub>-PHFBA<sub>400</sub>-PAA<sub>100</sub>. (THF-d<sub>8</sub>, ppm from TMS): 1.05 (CH<sub>3</sub>), 1.59 (CH<sub>3</sub>), 2.21 (CH<sub>2</sub>-CH), 4.16 (CH), 4.56 (O-CH<sub>2</sub>), 5.46 (CH-F), 12.26 (OH), 2.61 (1,4-dioxane), 6.12 (CH<sub>2</sub>=CH).



**Fig. S5:** Transmission FTIR spectrum of PAA<sub>100</sub>-PHFBA<sub>400</sub>-PAA<sub>100</sub>. 2972cm<sup>-1</sup> (CH<sub>3</sub>-CH<sub>2</sub>), 1714 cm<sup>-1</sup> (C=O), and 660 cm<sup>-1</sup> (CF<sub>3</sub>).



**Fig. S6:** Absorbance ATR spectra of the latex films: PAA<sub>100</sub>-PHFBA<sub>300</sub>-PAA<sub>100</sub> (red) and PAA<sub>100</sub>-PHFBA<sub>600</sub>-PAA<sub>100</sub> (black).

## Reference

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